

Surface Energy Properties of Yttrium Barium Copper Oxide Filled Polystyrene Composites

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Abstract

Micro crystalline ceramic powders of Yttrium Barium Copper Oxide [YBa₂Cu₃O₇] (YBCO) have been prepared by conventional ceramic preparation technique. X Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) studies revealed that YBCO particles are in micrometer range. Composites are prepared by mixing the ceramics with Polystyrene (PS) at different volume fractions of the materials. Melt mixing technique was carried out in brabender plasticorder at a rotor speed of 60 rpm for six minutes. Surface energy characteristics of the composites are calculated using contact angle measurements of the composites with water and methylene iodide. The results are quantitatively analyzed with Girifalco-Good empirical model and Wu's harmonic mean equations that provide unique insight into its properties. Various wettability parameters such as total solid surface free energy, work of adhesion, interfacial free energy and spreading coefficient etc. are analyzed. The work of adhesion and interfacial free energy, spreading coefficient, and Girifalco-Good's interaction parameter had changed with composition. The surface properties can be controlled over a given polymer-surface pair by governing the chemical structure, composition etc.

Keywords

Contact Angle; Surfaces; Yttrium Barium Copper Oxide; Polystyrene; Composites

Introduction

Many scientifically fascinating and technically important processes depend on the unique properties

of molecules between phases. A surface defined as the boundary between two phases; it might be more accurate to be called an interface, because two phases cannot exist without an interface. The surface of a phase or the interface between phases is a region of high energy relative to the bulk.

It is observed experimentally that a force is required to extend a liquid surface. The surface tension or interfacial tension ' γ ' is defined as the reversible work W_r , required to increase the surface of the liquid by a unit area. It is common to refer ' γ ' as the surface tension when fluid surface is discussed, and as surface free energy when solid surface is in discussion. Since surface tension is the force (per unit length) that opposes the stretch of the liquid film, it is a measure of intermolecular forces.

Contact angle measurements of solids are a widely accepted characterization technique for the measurement of intermolecular forces acting across the boundary. Using this technique, one can determine the surface free energy, interfacial free energy as well as polar and dispersion components of surface energy. In addition, information regarding hydrophobic-hydrophilic alterations, polar group orientations, etc. can be determined. Non-wettable solid surface is of great interest in the applications of microelectronics. Wettable solid surfaces are mostly used in applications such as biocompatibility, printing, coating and oil recovery, membrane for reverse osmosis, detergency,

ore flotation, and retention of pesticides on leaves. Composite preparation has been considered as an important route to fulfill several technological applications of polymeric materials. Plastics are of low density as well as good short-term chemical resistance but only with moderate resistance to environmental degradation (especially that caused by the photochemical effects of sunlight). Though they lack thermal stability, and have poor mechanical properties, but are easily fabricated and joined. Ceramics have great thermal stability and are resistant to most forms of attack (abrasion, wear, corrosion). Although intrinsically very rigid and strong because of their chemical bonding, they are all brittle and can be formed and shaped only with difficulty. In composites, materials are combined in such a way so as to enable us to make better use of their virtues while minimizing to some extent the effects of their deficiencies. The composite approach offers systematic solution to this challenging problem. Controlling the wettability of a surface has gained huge attention because wettability (hydrophobic, amphiphobic, and hydrophilic etc.) plays a crucial role in many natural and industrial applications, e.g. self-cleaning, water repellency, superhydrophobic coatings, intelligent textiles, infection of medical polymers and particle attraction in deoxyribonucleic acid (DNA) purification. Generally, the wettability of a solid surface is mainly caused by the chemical composition and structure asperities, which depends on surface energy and geometric structure. Enhancement on hydrophobicity of the composite is needed when used in microelectronics. As important as enhancement on hydrophobicity of polymer surfaces, controlling hydrophilicity of polymer surfaces is also an interesting issue because most polymers are hydrophobic in nature, which makes them unsuitable for important biomedical applications

Much chemistry is concerned with the short range wave-mechanical force responsible for chemical bond. The emphasis here is put on the less chemically specific attractions, often called Van der Walls forces that cause condensation of a vapor to a liquid. That is a combination of London dispersion forces, the wave mechanical force acting between both polar and non-polar materials, dipole-dipole interactions and hydrogen bonding between the test liquid and solid surfaces in contact. Recent developments in this area include the ability to measure dispersion interactions

with a surface force apparatus along with increasingly sophisticated theoretical analysis of the force expression. It is well established from the literature that contact angle measurements can be used in the calculation of surface energy. A liquid drop is inserted upon the solid surface and analysis on the drop shape is an effective way to measure contact angles and thereby determining surface energy. The principal assumptions are that the drop is symmetric about a central vertical axis: which means it is irrelevant to which the direction the drop is viewed. The drop is not in motion in the sense that viscosity or inertia plays a role in determining its shape: which means that interfacial tension and gravity are the only forces shaping the drop. Contact angles are explained by fitting a mathematical expression to the shape and tangent of the drop at the liquid-solid-vapor (LSV) interface line. The experimental drop of liquid is a sessile drop, a sitting drop, as in a drop of water resting on a table.

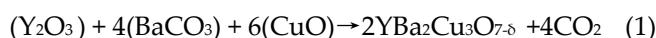
In the present work, we have synthesized YttriumBariumCopperOxide (YBCO) ceramic material and prepared composites out of it by mixing it with polystyrene. A detailed discussion of the structural mechanical and dielectric properties of (YBCO-PS) composites has been published elsewhere. In reference, a study has been reported on the particle size of the prepared (YBCO) and checked whether there was any size change with composite preparation. The average grain size of YBCO is 590 nm. Agglomeration or clustering seems to be absent in the composite structure. All the particles are seen to be neatly coated with polystyrene. The microstructure is dense and void free. Any size change with composite preparation was free from acquisition. In the present paper, the wetting properties of (YBCO-PS) composites have been discussed in detail.

Experimental

Preparation of YBCO

Solid-state reaction technique was adopted for the preparation of the material. The starting materials were BaCO_3 (Merck Ltd., Mumbai, India) Y_2O_3 (CDH, New Delhi, India) and CuO (Merck Ltd., Mumbai, India). In order to prepare 15 grams of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, 2.26952 grams of Y_2O_3 , 7.93356 grams of BaCO_3 and 4.79685 grams of CuO were required. The constituent oxides mixed in stoichiometric ratios (as in equation 1)

in an agate mortar were calcined at a temperature of 930°C , which was repeated twice. Calcinations promote the decomposition of carbonates leading to the formation of the desired phase of the superconducting YBCO compounds. By each intermediate grinding, the quality of the end product was expected to improve. Then the material was reground and sintered in air at 930°C for 15 hrs. The grinding and sintering was repeated in oxygen and finally the material was annealed in oxygen at 500°C for 10 hrs. Two stages were required to synthesize the 92K superconducting material. Firstly, the basic structure must be formed at the temperature above 700K . The tetragonal structure so formed is deficient in oxygen and does not possess superconducting properties. Accordingly the second part of the synthesis involves annealing under oxygen at a temperature 500°C . The arrangement of additional oxygen in the lattice causes a conversion from tetragonal to orthorhombic symmetry that supports superconductivity. During the annealing process, a structural transition of the 1-2-3 compound from tetragonal to orthorhombic crystal symmetry takes place with varying oxygen deficiency parameter 'δ' from 0.5 to zero where 'δ' is the variable oxygen content.



Polystyrene (PS)

In its structure the repeating unit has same chemical composition and the molecular weight of the unit as 104. A value of 2000 for 'n' represented in Fig 1(a) is the number of repeating units for the polystyrene used in this work. An average molecular weight of PS is 208000, and atactic in nature as in Fig. (b).

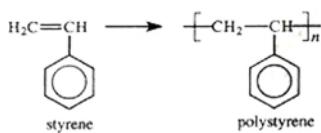


FIG. 1 (a) (REPEATING UNIT)

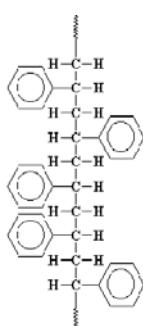


FIG. 1 (b)

FIG. 1(a) & (b) STRUCTURE OF POLYSTYRENE

Composite Preparation

The melt mixing technique was chosen to prepare the

composites because it is a solvent free technique. By melted at high temperature, molten polystyrene can easily penetrate between filler particles; which facilitate suitable mixing and allow avoiding air trapping into the composites. Consequently void free composites were obtained. (YBCO-PS) composites were prepared in a brabender plasticorder. The cavity for mixing in the instrument having an internal volume 40 cm^3 is fitted with two screw type rotors with variable speed. Filling the internal cavity with 90% of mixing charges ensures a constant ram pressure and a good mixing. The temperature of the internal mixer was raised to 180°C and then polymer was added; complete melting of polymer was ensured by a constant minimum torque and reattainment of the desired cavity temperature of 180°C . YBCO powder then added to the molten polymer was mixed for about 6 min at a rotor speed of 60 rpm. This time was sufficient to generate a steady state torque response, indicative of uniform dispersion of the components. The compositions of the fillers were 0% 10%, 20%, 30% and 40% by the volume fraction of the filler (YBCO). The mixed samples were compression molded into sheets of desired thickness by hydraulic press at a temperature of 180°C and a pressure of $120 \times 10^5 \text{ N/m}^2$. The composites named as YBCO10, YBCO20, YBCO30 and YBCO40, where 10, 20, 30 and 40 represent the volume of filler present in the composites.

Measurements

The morphology and microstructure of the composites were analyzed by means of high resolution scanning electron microscopy using a JEOL JSM 840. microscope. SEM (Scanning Electron Microscope) pictures of selected composites have been made to characterize the morphology of the composites.

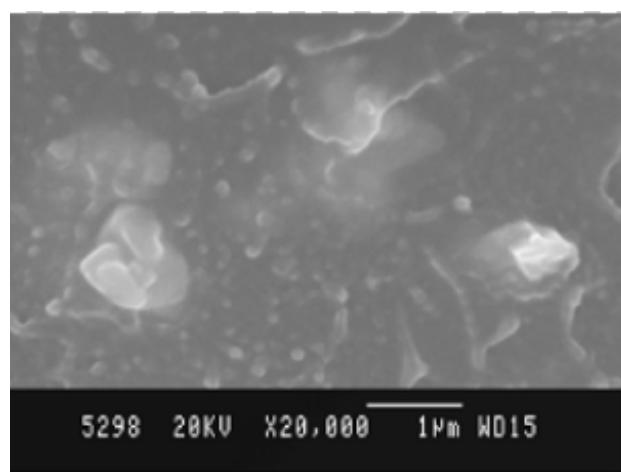


FIG. 2(a)

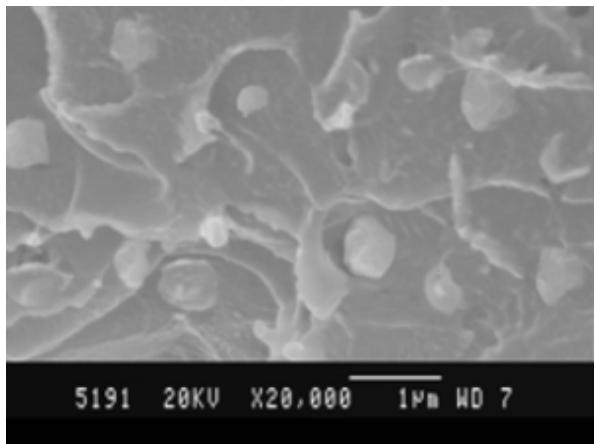


FIG. 2(b)

FIG. 2(a) AND 2(b) FRACTURE SURFACE VIEW OF YBCO20 AND YBCO40

Figs2 (a, b) shows the SEM images of the selected composites, which reveal that fillers are well dispersed and embedded rather uniformly through the PS matrix. The average particle diameter is found to be less than one micrometer in the two YBCO-PS composites. The filler particles are almost spherical in shape with irregular boundaries, which gives clear evidence to the (0-3) connectivity of the composites.

Contact Angle Measurements

Measurements have been done by a fully computer controlled instrument based on video capture of images and automatic image analysis to measure static, advancing and receding contact angles. Surface or interfacial tension of liquids, surface free energies and absorption of liquids into porous materials can be found by this instrument.

For solids, a static contact-angle setup using the sessile drop method was utilized. The setup consists of a micrometer-controlled syringe held in place above a moveable stage shown in Fig 3. Contact angles were

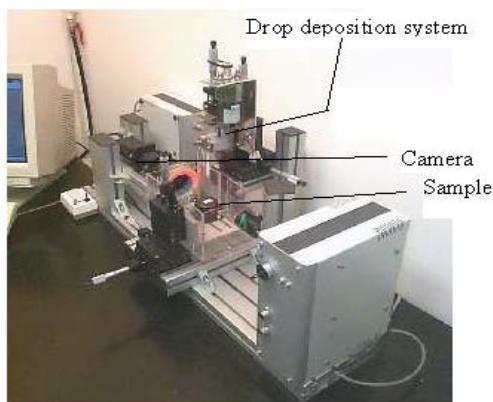


FIG. 3 TYPICAL APPARATUS FOR MEASURING CONTACT ANGLE

recorded using a goniometer equipped with a charge-coupled-device camera and using an image capture video program. Contact angles were measured by defining a circle around the drop and recording the tangent angle formed at the composite surface. Only deionized water is to be used with the syringe to access the hydrophobicity of the surface. Measurements are carried out with water (triply distilled) and methylene iodide (Kemphasol, Mumbai) on sample of size $1 \times 1 \times 2 \text{ cm}^3$ at room temperature. The volume of the sessile drop is maintained as $5\mu\text{l}$ in all cases using a micro syringe. The contact angle is measured within 45-60s of the addition of the liquid drop to the solid surface. Measurements are repeated six to ten times with different test pieces of the same sample for accuracy. The surface of the samples should be smooth and clean. The drop is allowed to reach equilibrium before the measurement is recorded and before evaporation occurs. Once the drop has been measured, the slide is moved to allow another drop to be placed on the sample surface. The same process is then repeated using methylene iodide

Theory and Calculations

The relationship between surface and interfacial energies determines to a large extent the wetting behaviour of a liquid on a solid surface and the phase morphology of mixtures of two or more phases. Many important and interesting technical phenomena are related to the spreading or wetting of liquids on solids. Fig 4 (a) shows a drop of liquid on solid surface and three interfacial tensions that govern the shape of the liquid. (γ_{sv}) is the interfacial tension between solid phase and vapor phase, γ_{sl} , is the interfacial tension between solid and liquid phase and (γ_{lv}) is the surface tension of the liquid or the interfacial tension between the liquid and the vapor phase.

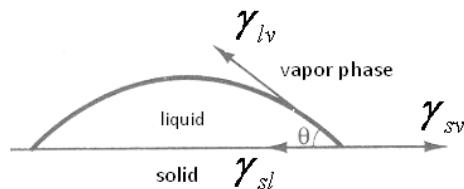
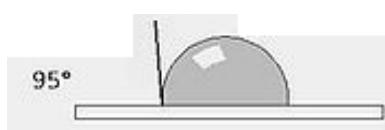


FIG. 4 (a)



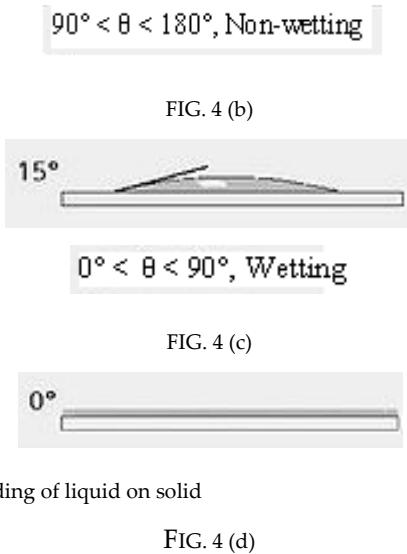


FIG. 4 (a-d) FORCES THAT CONTROL WETTING OF A SURFACE.

The angle between the solid surface and the tangent to the liquid surface at the contact point, the contact angle, may vary between 0 and 180°. The angle specifies the conditions for minimum energy according to the equation 3, which is a thermodynamic equilibrium condition for an ideal solid-liquid system.

Changes occur in Gibb's free energy dG when the drop spreads an infinitesimal amount,

$$dG = \gamma_{sl} dA - \gamma_{sv} dA = \gamma_{lv} dA \cos \theta \quad (2)$$

At equilibrium

$$dG / dA = 0$$

γ_{lv} and θ are directly measurable but γ_{sv} and γ_{sl} are not. Wetting behavior depends on interfacial and solid surface energy as well.

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (3)$$

where γ_{sv} , γ_{sl} , γ_{lv} are the interfacial energies between the phases solid-vapor, solid-liquid and liquid-vapor actually present in the system at the time of measurement.

For simplicity of the above equations γ_{sv} , is now onwards taken as (γ_s) , and γ_{lv} as (γ_l)

$\theta = 90^\circ$ may be defined as the boundary between non wetting ($\theta > 90^\circ$), and wetting ($\theta < 90^\circ$). Spreading is the condition in which the liquid completely covers the solid surface ($\theta = 0^\circ$). Relationships between the surface

energies and contact angle is a measure of the wetting behavior (Figure 4[b-d]) and spreading coefficient ' S_c '.

For spreading to occur it is necessary that ' S_c ' be positive. A necessary and sufficient condition for spreading is that the liquid-vapor interface energy be

less than solid vapor interfacial energy $\gamma_{lv} < \gamma_{sv}$.

Wettability Studies

The classic equation related to the surface energy of a solid in contact with vapour γ_{sv} or (γ_s) , liquid in contact with vapour, γ_{lv} , or (γ_l) , interfacial free energy between solid and liquid, γ_{sl} , and the contact angle (θ) due to Young given in equation 3. The extensive use of Young's equation reflects its general acceptance.

In the equation 3, (γ_s) and γ_{sl} are unable to be read by direct measurement. A plot of (θ) against surface tension for a homologous series of liquids, (γ_l) , can be extrapolated to give a critical surface tension γ_c , at which $\cos \theta = 1$. γ_c has been taken as an approximate measure of surface free energy γ_s , of the surface. However, a limitation of this consideration is that the precise value of γ_c , depends on the particular series of liquids used to determine it.

Semi Empirical Model

There are numerous methods to calculate the surface energy components employed by various researchers. These methods differ in several regards, such as derivation and assumptions, but most importantly they differ in the number of components or parameters which are equipped to analyze. The simpler methods containing fewer components simplify the system by lumping surface energy into one number, while more rigorous methods with more components are derived to distinguish between various components of the surface energy. In addition, the total surface energy of solids and liquids depends on different types of molecular interactions, such as dispersive (van der Waals), polar, and acid/base interactions, and so total surface energy considered being the sum of these independent components. Some theories account for more of these phenomena than other theories. These distinctions are to be considered when decision must be made on which

method is appropriate for the experiment at hand. The followings are a few commonly used such theories.

The Two Component Theories

The two component theories means the total surface energy consistsing of two components, namely dispersive and polar which would most likely be applicable to materials in which interactions of liquids and solids occur or not. The Owens/Wendt theory, the Fowkes theory, and Wu theory are the major ones among them. The Owens/Wendt theory, which deals with low energy solid surfaces, would be helpful in characterizing the interactions where the solids and liquids do not have a strong affinity for one. The Fowkes theory more suitable for higher energy solid surfaces, and since much of it is rooted in theories about adhesion, would likely be suitable for the characterization of interactions where the solids and liquids have a high affinity for one another, such as, logically enough, adhesives and adhesive coatings. The Wu theory is also essentially similar to the Owens/Wendt and Fowkes theories, in that it divides surface energy into a polar and a dispersive component. The primary difference is that Wu uses the harmonic means rather than the geometric means of the components of surface tensions, and subsequently the use of more rigorous mathematics is employed. They are derived from the combination of Young's relation, which relates the contact angle to the surface energies of the solid and liquid and to the interface tension, and Good's equation. The Fowkes theory is derived in a slightly different way from the Owens/Wendt theory, although the Fowkes theory's principle equation is mathematically equivalent to that of Owens and Wendt.

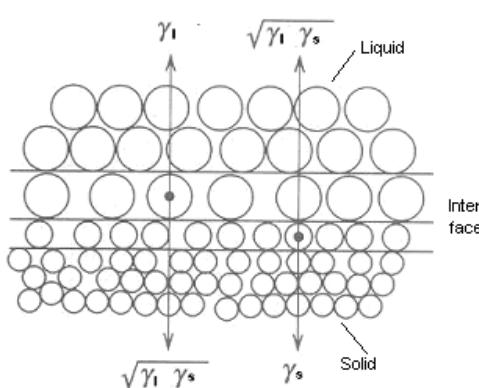


FIG. 5 GOOD-FOWKES MODEL FOR CALCULATING INTERFACIAL TENSION

A model as in Fig 5 that has proved to be very stimulating to research on contact angle phenomena begins with the proposal put forward by Girifalco and Good.

It is assumed that the two phases are mutually entirely immiscible and γ_{sl} is related to γ_s and γ_l through geometric mean law relationship *i.e.*

γ_{sl} is equivalent to $(\gamma_s \gamma_l)^{1/2}$ through the interaction parameter ϕ in equation (4)

Interfacial free energy should obey the equation

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\phi(\gamma_l \gamma_s)^{1/2} \quad (4)$$

In order to include other interactions such as dipolar or hydrogen bonding, many semi empirical approaches have been tried, including adding terms to the above equation or modifying the definition of ' ϕ '.

In order to verify Wu's approach of harmonic mean, by means of the inclusion of the two component of surface tension, two liquids of dissimilar polar types are to be selected. One polar liquid (water) and other non polar liquid (methylene iodide-MI) are selected for our study. The interfacial tension arises mainly from disparity in the polarities of the two phases. The prescribed equation can also be used to calculate the surface tension and polarity of polymers or organic solids from contact angle data. Wu's harmonic mean equations are

$$(1 + \cos(\theta_w))r_w = 4 \left[\frac{r_w^d r_s^d}{r_w^d + r_s^d} + \frac{r_w^p r_s^p}{r_w^p + r_s^p} \right] \quad (5)$$

$$(1 + \cos(\theta_m))r_m = 4 \left[\frac{r_m^d r_s^d}{r_m^d + r_s^d} + \frac{r_m^p r_s^p}{r_m^p + r_s^p} \right] \quad (6)$$

TABLE 1 COMPONENTS OF SURFACE ENERGY OF WATER AND METHYLENE IODIDE

Liquid	Total Surface tension (mj/m ²)	Dispersive component (γ^d) (mj/m ²)	Polar Compo (mj/m ²)
Water	72.8	21.8	51
Methylene Iodide	50.8	49.5	1.3

where the superscripts d and p stand for contributions due to dispersion and polar forces, respectively. Data for water and methylene iodide (MI) taken from the literature are reported in Table 1

Dispersive and polar component of surface energy of the composites γ_s^d and γ_s^p for different compositions of YBCO-PS composites are determined by solving equations (5) and (6) with the help of a computer program in C language. According to Owens-Wendt theory, the total solid surface free energy is represented in units of (mj/m²) as in equation (7)

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (7)$$

The work of adhesion, W_A , was calculated using the equation

$$W_A = (1 + \cos \theta) \gamma_l \quad (8)$$

Where γ_l is the surface tension of the liquid used for the contact angle measurement.

The interfacial free energy, γ_{sl} was calculated from Dupres equation

$$\gamma_{sl} = \gamma_s + \gamma_l - W_A \quad (9)$$

Girifalco – Goods interaction parameter, ϕ , between the polymer and the liquid was determined using the equation given below.

$$\phi = \frac{(1 + \cos \theta) \gamma_l}{2(\gamma_l \gamma_s)^{1/2}} \quad (10)$$

The spreading coefficient of liquid with respect to solid surface is given by

$$S_{l/s} = \gamma_s - \gamma_l - \gamma_{sl} = S_c \quad (11)$$

The total surface energy γ_s along with its dispersive and polar components are reported in (Table 2).

Results and Discussion

The wetting behaviour of the composites with respect to water and methylene iodide is analyzed which focuses on the effect of volume percentage of the filler

on wetting characteristics such as work of adhesion, total surface free energy, interfacial free energy and spreading coefficient. The hydrophobic nature of the composites is found to be increased with the addition of fillers.

Contact Angle Variations

The composites hold higher contact angles with water and lesser with methylene iodide compared to neat PS.

TABLE 2 COMPONENTS OF SURFACE ENERGY OF YBCO-PS in units of (mj/m²)

Name	CA (water ⁰)	CA (m. I ⁰)	γ_s^d	γ_s^p	γ_s
PS	85	45	34.95	6.699	41.649
YBCO10	86	44	35.48	6.49	41.97
YBCO20	86.5	43.5	36.047	6.19	42.237
YBCO30	87	43	36.36	5.99	42.35
YBCO40	88	42	36.7	5.81	42.51

A high contact angle indicates a low degree of wetting. While a low contact angle indicates a high solid surface energy or chemical affinity, and a high or sometimes complete degree of wetting. Even though the water absorption percentage of PS is 0.05, the addition of fillers increases the hydrophobic nature to a higher value. The increase in contact angle value can also be compared with the increase in surface roughness of the polymer surface. The roughness of the sample surfaces increases by the addition of YBCO.

Surface Free Energy

TABLE 3 PROPERTIES OF YBCO-PS RELATED TO WATER in units of (mj/m²)

Name	Con Ang (water ⁰)	W_A	γ_{sl}	S_c	ϕ_w
PS	85	79.14	35.35	-66.5	0.7187
YBCO10	86	77.88	36.97	-67.8	0.7045
YBCO20	86.5	77.24	37.797	-68.4	0.6965
YBCO30	87	76.61	38.54	-69	0.689
YBCO40	88	75.34	39.97	-70.3	0.677

Surface energy γ_s , is the energy associated with the interface between two phases. The solid surface is rich in hydrocarbon molecule. The forces held between hydrocarbons together are much stronger than the force that acts between molecules at interfacial layer and consequently water on a hydrocarbon surface remains in non wetting form. Surface free energy based on contact angle values of water and methylene iodide is reported in Table 2. It can be seen that the surface free energy increases with filler content. Thus the surface energy of the composites increases from 41.64, which is the surface energy of the neat PS at room temperature.

This change which occurs over the whole range of the concentration must result from an increase in free energy due to the mixing of two components at the interface. The dispersive (non polar) component of surface energy is found to increase and polar component decreases with filler content whereas, insignificant variation in total surface energy. YBCO-PS composites have almost equal surface free energy values, which suggests that the natures of forces acting at the surface of these two composites are approximately the same. The strength of dispersion forces tends to increase with increase in molecular weight. Larger atoms like YBCO have larger electron cloud which is not easier to be polarized.

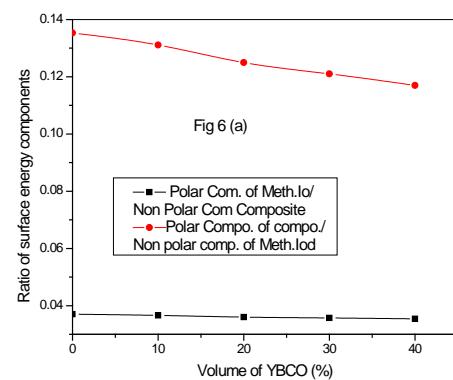
TABLE 4 PROPERTIES OF YBCO-PS RELATED TO METHYLENE IODIDE IN UNITS OF (mj/m²)

Name	C. A (m.I ⁰)	W_A	I. E	S_c	ϕ_m
PS	45	86.72	5.73	-14.881	0.9428
YBCO10	44	87.34	5.43	-14.26	0.9457
YBCO20	43.5	87.64	5.397	-13.96	0.946
YBCO30	43	87.95	5.2	-13.65	0.948
YBCO40	42	88.55	4.76	-13.05	0.952

Work of Adhesion

The work of adhesion, (W_A) which is the work required to separate the composite surface and the liquid drop, changes with filler concentration. The

values of work of adhesion related to both liquids are presented in the third column of Table 3 and 4. In surface science, the term 'adhesion' almost always refers to dispersive adhesion. For small contact angle, adhesion is large, due to larger surface area between solid and liquid. The possibility of polar- non polar interaction across the surface is a measure of adhesion between the test liquid and solid surface. So for maximum adhesion the ratio of polar to non polar component across the interface should be same.



This ratio is less than one for M I – liquid and for composite- M I as in Figure 6(a). This ratio is greater than one for water-composite systems and less than one for composite water system as in Fig 6(b). The trend is same but in opposite manner because of the inherent property of water as polar and MI as non polar. Generally work of adhesion can be correlated to filler matrix interaction. The effective dispersion of filler into matrix has caused a decrease in work of adhesion, and increase in hydrophobic nature.

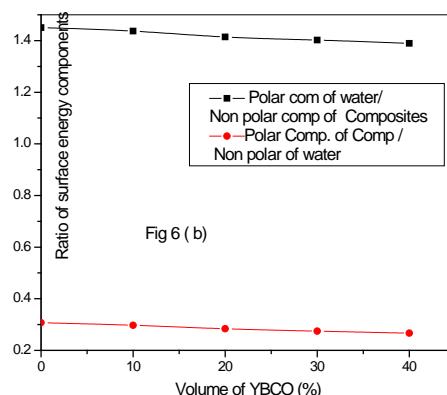


FIG. 6(a-b) SURFACE ENERGY RATIOS OF COMPOSITES

Interfacial Energy

The interfacial energy between the composites and

liquids is reported in the fourth column of the Table 3 and 4. The solid and liquid configuration of the surface adapts itself to minimize its excess energy. The dipoles orient themselves in such a way so as to give minimum surface energy. Ions can be fitted on the surface with relatively low energy only if they are highly polarizable ions, such that the electron shells can be distorted to minimize the energy increase produced by the surface configuration. Consequently highly polarizable ions tend to form the major fraction of the surface layer. The interfacial energy is defined as the energy necessary to form a unit area of the new interface in the system. This is always less than the sum of the separate surface energies of the two phases, since there is always some energy of attraction between the phases. It may be any value less than this sum, depending on the mutual attraction of the two phases. The interfacial free energy γ_{sl} between the composite surface and the test liquids, water and methylene iodide behaves in opposite manner. With water the interfacial free energy increases markedly and with methylene iodide it decreases compared to neat PS. The different kinds of intermolecular forces such as dispersion, hydrogen bonding and polar may not equally contribute to solid-solid, liquid-liquid and solid-liquid interactions. For water composite system, the potential function of water contains important hydrogen bonding contributions absent in MI-composite system. The effects of polar-polar and polar non polar interactions are not contributive to an additive manner with the two composite systems (M.I-composite system, Water-composite systems). There has been considerable theoretical development in the treatment of interfacial tension and work of adhesion. As illustrated in Fig 5, schematic model for interfacial tension, ' γ_{sl} ' may be regarded as the sum of work to bring solid and liquid molecules to their respective solid-vapour and liquid-vapour interface less than the free energy of interaction across the interface. This is determined through Wu's harmonic mean relationship.

Spreading Coefficient

The spreading coefficient ' S_c ' implies that a liquid will spontaneously wet and spread on the solid surface if the value is positive whereas, a negative value of ' S_c ' implies the lack of spontaneous wetting. This means the existence of a finite contact angle i.e. $\theta > 0$. Spreading coefficient is positive if spreading is accompanied by a decrease in free energy. A liquid of

high surface tension would not be expected to spread on one of much lower surface tension; thus ' S_c ' is negative with water and methylene iodide.

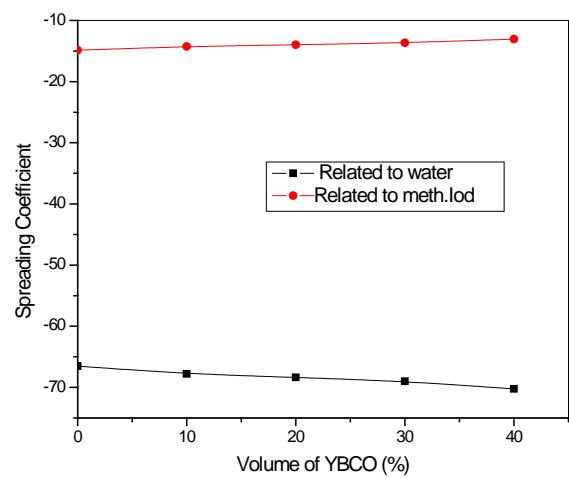


FIG.7 VARIATION OF SPREADING COEFFICIENT

The spreading coefficients of composites for water and methylene iodide are given in the fifth column of Table 3 and 4 respectively. From Fig 7, it can be noted that the wetting due to methylene iodide and water reverses upon filler addition.

By means of comparison between water and methylene iodide, the less negative value is given by methylene Iodide which means that it is a better wetting agent for the current composites. Thus wetting has decreased for water with the addition of fillers indicating more hydrophobic nature of the composites and which in turn reduces the water absorption capacity of host matrix, polystyrene. The polar-polar interactions across the interface is a measure of wetting. The polar component of surface tension decreasing with filler loading is the peculiarity of non wetting surfaces

Interaction Parameter.

Girifalco-Good's interaction parameter (ϕ) is calculated and plotted in Figure 8 to provides a good understanding of the degree of interaction between the test liquid and the polymer surface. Empirically, the value of (ϕ) changes from 0.5 to 1.15. In this type of calculation Skapski type of approach is used, all interactions except the nearest neighbour interactions are neglected. Among the different kinds of nearest neighbour intermolecular forces (dispersion, polar, hydrogen bonding etc), the component that is

contributive to water composite system may not be so much effective in the other case. The values are given in the last column of Table 3 and 4. A higher value indicates greater interaction. ϕ_w and ϕ_m are the Girifalco Good's interaction parameters due to water and methylene iodide respectively. Thus based on Girifalco-Good's interaction parameter, ϕ_w and ϕ_m , it can be suggested that the interaction parameter is proportional to work of adhesion and spreading coefficient.

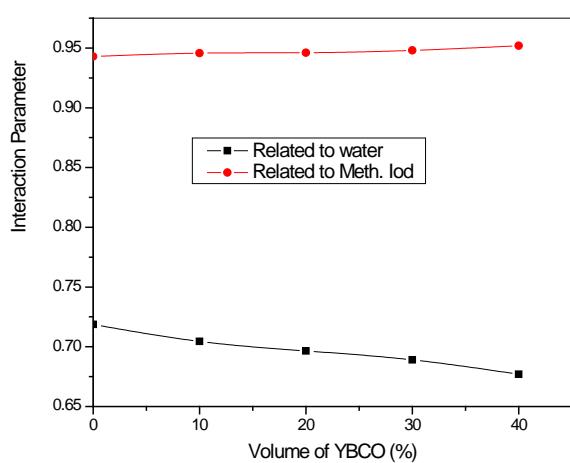


FIG. 8 INTERACTION PARAMETER WITH WATER AND METHYLENE IODIDE

Conclusions

The contact angle with water and methylene Iodide get changed by the addition of ceramic filler to polystyrene matrices. The nature of surface forces appears to be the same in all YBCO-PS composites. The hydrophobic nature of PS increases with composite formation. The solid surface free energy of the composites increased and thereby decreasing work of adhesion in water composite system

Methylene Iodide shows less negative value for the spreading coefficient than water and it is a good wetting agent than water. Adhesion between composite and water is totally absent. Finally the nature of the particle and particle dispersion in the matrix has affected the various parameters analyzed as each one of them changed according to the filler loading.

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